THE FORMATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) DURING PULPING

Project F01708

Report 4

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MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

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INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

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By

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The Formation of Volatile Organic Compounds (VOCs) During Pulping

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EXECUTIVE SUMMARY

The emission of volatile organic compounds (VOCs) in pulp and paper mills has been an environmental concern. VOCs were mainly formed in the pulping process in kraft mills. These VOCs are soluble in water and become an important source of biodegradable organic compounds to increase the biochemical oxygen demand (BOD). Furthermore, these species can also be released into the atmosphere at the process temperatures of kraft mill streams. The quantity of VOC formed (VOC yield) during pulping was not reported in the literature. Therefore, research on VOC yield during various pulping conditions using different raw materials can provide useful information to estimate VOC formation in pulp mills.

This study measured the time-dependent concentration profiles of major water-soluble volatile organic compounds (VOCs), i.e., methanol, acetone, and methyl ethyl ketone (MEK), during conventional pulping processes of southern pine, birch, and kenaf in a laboratory digester. These VOC species were mainly formed in the early stages of the cooking. The study shows that more methanol is formed in kraft pulping than in soda pulping. The study also verifies the conclusion found in the literature that hardwood pulping produces more methanol than softwood. Kinetic analysis indicates that the overall methanol formation reaction follows Arrhenius kinetics well. The catalyst, anthraquinone, increased the methanol formation in softwood kraft pulping, but reduced methanol formation in kraft hardwood pulping.

From the data obtained, this study also developed an empirical methanol formation model in conventional laboratory pulping that can be used for mill methanol formation estimations. Initial mass balance was obtained using the model developed. Future study is needed to obtain lignin demethylation kinetics for better prediction of methanol formation using the developed model.

INTRODUCTION

The formation of volatile organic compounds (VOCs), such as methanol and methyl ethyl ketone (MEK), during kraft pulping processes has been an environmental concern. These VOCs are soluble in water and become an important source of biodegradable organic compounds to increase the biochemical oxygen demand (BOD). Furthermore, these species can also be released into the atmosphere at the process temperatures of kraft mill streams. With the increasingly restrictive environmental regulations such as the Cluster Rule [1] by the U.S. Environmental Protection Agency, many VOCs are now on the list of hazardous air pollutants (HAPs) that are required to be controlled. The knowledge of VOC formation during the pulping process is limited. The quantity of VOC formed (VOC yield) during pulping was not reported in the literature. The effects of pulping conditions and catalyst on the VOC yield during pulping have not been studied. Therefore, research on VOC yield during various pulping conditions using different raw materials can provide useful information to estimate the VOC formation in pulp mills. The knowledge gained can help to develop technologies to reduce VOC emission at its source, i.e., during pulping.

Methanol has been identified as the main alcohol in pulp mill process streams [2-4]. A list of various VOCs present in pulp mill streams was summarized by Bethge and Ehrenborg [5] and Blackwell et al. [6]. According to Clayton [7], methanol could be formed by the rapid alkaline hydrolysis reaction of 4-O-methylglucuronic acid residues in hemicellulose (or hydrolyzation of xylan). Although methanol can also be formed through the demethylation of methoxyl groups in lignin [6, 8], the amount of methoxyl groups that can be demethylated is very small [8]. Therefore, it is reasonable to assume that the majority of methanol is formed through the hydrolyzation of xylan [7, 8]. Wilson and Hrutfiord [2] conducted a study on the reaction mechanism of VOCs using mill samples and analytical grade chemicals. They proposed that fermentation is the main formation pathway to all alcohol except methanol, and methyl ketones are formed by air oxidation of wood extractives followed by a reverse alcohol condensation. Later, Wilson et al. [9] studied the effect of wood species on the formation of VOCs in pulping and concluded that hardwood can yield many more VOCs than softwood.

The objective of the present study is to quantify VOC yields from different pulping processes using various raw materials. The concentrations of methanol, acetone, and methyl ethyl ketone (MEK) during each cooking process were obtained by analyzing the cooking liquor samples collected during various stages of pulping. The information obtained can be used to develop VOC formation model for the prediction of VOCs released in pulp mills.

EXPERIMENTAL

The pulping experiments were carried out in a laboratory batch digester (ME&K). Conventional pulping processes were employed in this study. The load of each batch cooking was 800 grams of oven-dried (O.D.) chips. Four types of raw materials were used in this study, i.e., southern pine (softwood), birch (hardwood), and kenaf bast and kenaf core (nonwood). Southern pine and birch were pulped separately by both kraft and soda processes, with and without a catalyst, anthraquinone (AQ). Kenaf bast and core were pulped separately using soda-AQ process only. The detailed pulping conditions are listed in Table I. After the addition of the chips and cooking liquor, the temperature of the digester was raised from room temperature to 100°C in 20 minutes. Then it was brought to 170°C in an hour, and maintained at 170°C for two hours. After the completion of the cooking, the digester was cooled to room temperature by draining the black liquor. The pulp was thoroughly washed before the handsheets were made for kappa number and viscosity analysis. The final kappa numbers of fibers from all the cooking processes are listed in Table II.

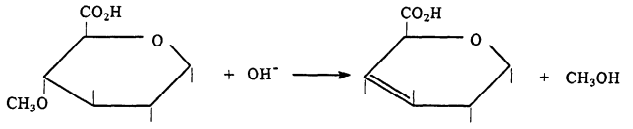
During each cooking process, a small amount (15 mL) of cooking liquor was collected at about 15-20-minute intervals after the temperature reached 100°C. The concentrations of methanol, acetone, and methyl ethyl ketone (MEK) in the collected liquors were analyzed using an indirect headspace gas chromatographic method that we developed [4]. We also determined the absorption of dissolved lignin in cooking liquor by UV spectrophotometry [10].

RESULTS AND DISCUSSIONS

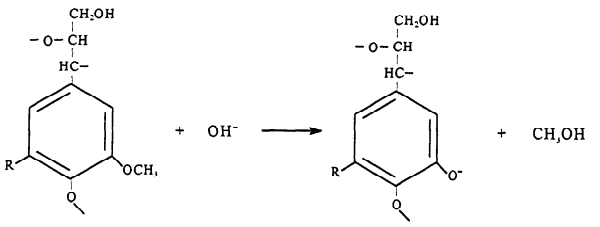
The VOCs in the kraft mill condensate streams, especially those most quoted in the literature [5, 6], include alcohols, ketones, phenolics, terpenes, and organic sulfur compounds. The composition of VOCs formed during pulping is related to the wood species and the pulping process employed. For example, a very significant amount of α-pinene was formed during softwood cooking. For kraft pulping, it was found that dimethyl sulfide is a dominant malodorous organic compound remaining in the cooking liquors [4]. The amount of methyl mercaptan (MM) is not significant in the solution because of its low boiling point. Methanol, acetone, and MEK were the major water-soluble volatile organic compounds found in the cooking liquors from both kraft and soda pulping process. In this study we found that methanol concentration in the cooking liquors could reach 1000 mg/L. The amounts of acetone and MEK were relatively low compared to methanol, about 2 to 8 mg/L in the cooking liquors. The other water-soluble volatile compounds, such as ethanol, were not significant in the black liquors.

Methanol Mass Balance and Formation Model

The purpose of chemical pulping is to separate fibers that consist of cellulose and hemicellulose by dissolving wood lignin in the cooking liquor through the so-called delignification process. During a pulping process, methanol can be formed mainly through the degradation of 4-O-methyl-D-glucuronoxylans in hemicellulose through hydrolysis [7] as shown in reaction (1a). According to Sarkanen et al. [8], methanol formation through the demethylation of the aromatic methoxyl groups in lignin structure, as shown in reaction (1b), is insignificant.



(1a)



(1b)

In this study, we measured the methanol concentrations in the cooking liquors collected at various stages of all the pulping experiments. Fig. 1 shows the methanol concentration and UV absorption of the dissolved lignin measured as a function of cooking time in a kraft cooking of southern pine (softwood). The results show that the methanol concentration increased as temperature increased. It was found that the formation of methanol increased along with dissolved lignin during the first 1.5 hours of the pulping process. After that, the dissolved lignin concentration continued to increase, while the methanol content leveled off. Reaction (1a) was supported by xylan hydrolysis studies using model xylan compounds [7]. The methoxyl groups from the 4-O-methyl-glucuronoxylan was found close to zero after 2 hours of hydrolysis reactions [7]. We can carry out a mass balance calculation to estimate the methanol yield based on the assumptions of 100% hydrolysis of methoxyl groups in xylan. The amount of 4-O-methyl-glucuronic acid $m_{me\text{-}glu\text{-}acid}$ in a wood can be expressed as the xylan content x_{xylan} times the ratio of 4-O-methyl-glucuronic acid to xylose $R_{me\text{-}glu\text{-}acid}$,

$$m_{me-glu-acid} = x_{xylan} \cdot R_{me-glu-acid} \cdot m_{wood} \tag{2}$$

According to reaction (1a), 1 M of 4-O-methyl-glucuronic acid forms 1 M of methanol. Therefore the amount of methanol formed would be:

$$m_{MeOH\text{-}xylan} = \frac{M_{MeOH}}{M_{me-glu-acid}} \cdot m_{me-glu-acid} \cdot f\,, \tag{3}$$

where $M_{MeOH} = 31$ and $M_{me\text{-}glu\text{-}acid} = 186$ are the molecular weight of methanol and the 4-O-methyl-glucuronic acid in wood xylan, respectively. f is the fraction of the 4-O-methyl-glucuronic acid hydrolyzed and is assumed to be equal to 1 in this study. The methanol concentration (mg/L) in cooking liquor can be expressed as

$$\left[C_{MeOH-xylan}\right] = \frac{m_{MeOH-xylan}}{R_{LW} \cdot m_{wood}} \times 10^6 = \frac{M_{MeOH}}{M_{me-glu-acid}} \cdot \frac{f \cdot x_{xylan} \cdot R_{me-glu-acid}}{R_{LW}} \times 10^6, \tag{4}$$

where R_{LW} is the liquor-to-wood mass ratio and the density of the cooking liquor is assumed equal to 1 kg/L, same as water.

Table III lists the sample calculations of methanol concentration using Eqn. (4) for the southern pine (softwood) and white birch (hardwood). The xylan content x_{xylan} and the ratio of the 4-O-methyl-glucuronic acid to xylose $R_{me\text{-}glu\text{-}acid}$ listed in the Table are based on the data given by Biermann [11] and Fengel and Wegener [12], respectively. The calculated concentrations of methanol formed from hemicellulose degradation through hydrolysis reactions in the cooking liquors of southern pine and birch are 937 and 781 mg/L, respectively. The table also lists the experimentally measured methanol concentrations (averaged over kraft, kraft-AQ, and soda-AQ processes) in the final cooking liquors in this study. The calculated methanol concentrations account for 70% and 77% of those measured in birch and pine liquors, respectively. The unaccounted methanol must be formed by the demethylation of methoxyl groups in lignin.

Similar to the derivation of methanol formation from 4-O-methyl-glucuronic acid in xylan, we can derive a mathematical model to predict methanol formation from lignin based on reaction (1b). As shown in Eqn. (5), the model takes the following facts into consideration: (1) softwoods contain only coniferyl alcohol, while hardwoods contain both coniferyl (50-75%) and sinapyl alcohols (25-50%) [11]; (2) sinapyl alcohol contains two methoxyl groups while the coniferyl alcohol only has one, as shown in Fig. 2; and (3) the reaction rates of the first and the second methoxyl groups of sinapyl lignin are different.

$$m_{MeOH-lignin} = M_{MeOH}\left(q_c \frac{m_{lig-Conf}}{M_{lig-Conf}} + (q_{s1} + q_{s2}) \frac{m_{lig-Sinp}}{M_{lig-Sinp}} \right)$$

$$= M_{MeOH}\left(\frac{q_c \cdot R_{Conf-alcoh}}{M_{lig-Conf}} + \frac{(q_{s1} + q_{s2}) \cdot R_{Sinp-alcoh}}{M_{lig-Sinp}} \right) x_{lignin} \cdot m_{wood}, \qquad (5)$$

where $M_{lig\text{-}Conf} = 177$ and $M_{lig\text{-}Sinp} = 198$ are the molecular weights of lignin for coniferyl and sinapyl alcohols, respectively; q_c, q_{s1}, and q_{s2} are the fractions of coniferyl methoxyl groups, the first and second methoxyl groups of sinapyl lignin demethylated, correspondingly; and x_{lignin} is the lignin content in the wood. The methanol concentration (mg/L) in a cooking liquor contributed by lignin demethylation can be expressed as

$$\left[C_{MeOH-lignin}\right] = \frac{m_{MeOH-lignin}}{R_{LW} \cdot m_{wood}} \times 10^6$$

$$= M_{MeOH}\left[\frac{q_c \cdot R_{Conf-alcoh}}{M_{lig-Conf}} + \frac{(q_{s1} + q_{s2}) \cdot R_{Sinp-alcoh}}{M_{lig-Sinp}}\right] \cdot \frac{x_{lignin} \times 10^6}{R_{LW}} \quad (6)$$

According to Sarkanen et al. [8] wood lignin demethylation reaction consists of a rapid phase followed by a slower phase. Sarkanen et al. [8] studied various wood lignin demethylation reactions at a temperature range of 170-200°C with alkali concentration of 5-15%. It is obvious that the reaction rates of the first and the second methoxyl groups in sinapyl alcohol lignin of hardwood are different. This difference is neglected (or $q_{s1} = q_{s2}$) for simplification in the present calculation because limited data are available in the literature about the reaction rates of sinapyl lignin methoxyl groups. Based on the experimental data of Sarkanen et al. [8], we assumed that the fractions of methoxyl groups in sinapyl lignin demethylated are about 2.7% (or $q_{s1} = q_{s2} = 0.027$) for estimation of methanol formation in pulping of birch (hardwood). Because softwood lignin demethylation data are not available and softwood (pine or coniferyl lignin) is usually more difficult to delignin (has a slow reaction rate) than hardwood (e.g., birch), 1.5% is arbitrarily assumed ($q_c = 0.015$) for estimation.

The calculated concentration of methanol formed from lignin demethylation in the cooking liquors using Eqn. (6) for southern pine and birch are 255 and 197 mg/L, respectively, as listed in Table IV. The lignin content x_{lignin} and the ratios of coniferyl and sinapyl alcohol to lignin $R_{Conf-alcoh}$ and $R_{Sinnf-alcoh}$, respectively, are from Biermann [11]. The calculation results shown in Table IV suggest that with the assumption of only 2.7% and 1.5% lignin demethylation (for birch and pine, respectively), lignin demethylation contributes to about 20% of the methanol formed in pulping. In other words, though lignin demethylation is insignificant as suggested by Sarkanen et al. [8], its contribution to methanol formation cannot be neglected.

By combining Eqs. (4) and (6), we can obtain an empirical mathematical model to estimate the methanol concentration in the final pulping spent liquor.

$$[C_{MeOH}] = \frac{m_{MeOH} \times 10^6}{R_{LW} \cdot m_{wood}} = [C_{MeOH-xylan}] + [C_{MeOH-lignin}]$$

$$= \left[\frac{f \cdot R_{me-glu-acid}}{M_{me-glu-acid}} \cdot x_{xylan} + \left(\frac{q_c \cdot R_{Conf-alcoh}}{M_{lig-Conf}} + \frac{(q_{s1} + q_{s2}) \cdot R_{Sinp-alcoh}}{M_{lig-Sinp}} \right) \cdot x_{lignin} \right] \frac{M_{MeOH} \times 10^6}{R_{LW}} \quad (7)$$

Table V lists the methanol mass balance based on calculations using Eqns. (4), (6), and (7) and the experimentally measured data. We found that all of the methanol was accounted for except for about 10%. Considering the multiple estimation of the various parameters adopted from the literature and approximations taken to simplify the calculation, the model provided a very good empirical prediction.

Methanol Formation Reaction Rate

Since xylan hydrolysis contributes to about 75% of the methanol formed during pulping (with the assumption of 100% methoxyl group hydrolyzed), we can use the rate of xylan hydrolysis reaction (1a) to represent the overall methanol formation reaction rate for simplification as follows,

$$\frac{d[C_{MeOH}]}{dt} = -k[C_{CH_3O^+}] \cdot [C_{OH^-}]. \quad (8)$$

The methoxyl concentration is equal to its initial concentration minus the methanol concentration $[C_{MeOH}]$, i.e., $[C_{CH_3O^+}] = C^0_{CH_3O^+} - [C_{MeOH}]$. The hydroxide concentrations $[C_{OH^-}]$ in the cooking liquor was found to follow an exponential decay function, in agreement with those reported by Liaw and Krishnagopalan [13]. Eqn. (9) is a regression obtained hydroxide concentration profile for a kraft softwood pulping process shown in Fig. 1.

$$[C_{OH^-}] = 0.11 + 1.07 \exp\left(-\frac{t}{29.0}\right) = 0.11 + 1.07 \exp\left(-\frac{T-100}{24.86}\right) \quad (9)$$

Fig. 1 also shows a typical methanol concentration profile at various stages of a kraft softwood pulping experiment we conducted. To obtain an analytical solution for k, we used a Boltzmann function (expressed in Eqn. (10)) to fit the measured methanol concentration.

$$[C_{MeOH}] = C_T + \frac{C_0 - C_T}{1 + \exp\left(\frac{t - t^*}{\Delta t}\right)}, \tag{10}$$

where C_T = 1000 mg/L and C_0 = 248 mg/L and are the final and the initial methanol concentrations, respectively, obtained from curve fitting for this particular experiment as shown in Fig. 1; and t^*=71.4 and Δt=11.4 are two time parameters of the Boltzmann distribution derived from regression. By taking the derivative vs. time of Eqn. (10), we have

$$\frac{d[C_{MeOH}]}{dt} = \frac{\exp\left(\frac{t - t^*}{\Delta t}\right)}{\left[1 + \exp\left(\frac{t - t^*}{\Delta t}\right)\right]^2} \cdot \frac{C_T - C_0}{\Delta t} = \frac{(C_T - [C_{MeOH}])([C_{MeOH}] - C_0)}{C_T - C_0} \cdot \frac{1}{\Delta t} \tag{11}$$

Combining Eqns. (8) and (11) with the assumption that $C^0_{CH_3O^+} = C_T$, we have

$$k = \frac{([C_{MeOH}] - C_0)}{(C_T - C_0) \cdot \Delta t} \cdot \frac{1}{[C_{OH^-}]} \tag{12}$$

Since both the methanol and hydroxide concentrations are directly related to the pulping temperature, we can find the methanol formation reaction rate k as a function of temperature for the data presented in Fig. 1. Furthermore, we also can express the reaction rate k in the Arrhenius form as shown in Eqn. (13),

$$k = Z \cdot \exp(-\frac{E_A}{RT}) = \frac{([C_{MeOH}] - C_0)}{(C_T - C_0) \cdot \Delta t} \cdot \frac{1}{0.11 + 1.07 \exp\left(-\frac{T - 100}{24.86}\right)} \tag{13}$$

We conducted a linear regression analysis for the calculated reaction rate k in a temperature range of 100–170°C as shown in Fig. 3. We found that the natural logarithm of k vs. the inverse of temperature in Kelvin fits a straight line very well, suggesting that the reaction follows Arrhenius kinetics. From the regression results, we can obtain the reaction activation energy E_A = 1.2914x10^8 J/mol and the kinetic pre-exponential factor Z = 7.1528x10^{14}. We found that for all the pulping processes conducted in this study, the overall methanol formation reactions follow Arrhenius kinetics.

We would like to point out that the above analysis is an empirical analysis with the assumption that all the methanol is formed through hemicellulose hydrolysis and the hydrolysis reaction is homogeneous. Clearly, the diffusion of hydroxide in the cooking solution into a wood chip is an important factor in the actual heterogeneous pulping reactions. Furthermore, large errors may occur in this type of analysis due to limited measurements taken during the temperature ramping period of the pulping process as well as the sampling and measurement uncertainties. Therefore, quantitative comparisons of the activation energies of methanol formation reactions among various pulping processes are not very meaningful and were not conducted in this study. However, the above estimation can provide qualitative information about methanol formation during a pulping process.

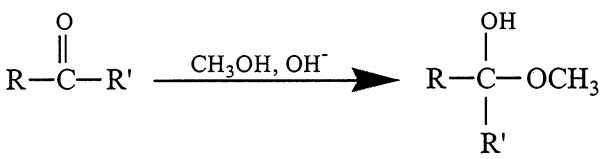
Comparisons Between Softwood and Hardwood

Figures. 4 and 5 show the concentration profiles of VOCs during kraft and soda pulping of softwood and hardwood. We found that the methanol concentration profiles are almost identical for both except that more methanol is produced in hardwood cooking than in softwood cooking. More methanol formation was also reported by Wilson et al. [9]. Hardwood has a higher content of 4-O-methyl-D-glucuronoxylans in hemicellulose than softwood does, and hardwood lignin has more methoxyl groups than softwood lignin does [11]. Softwoods contain only coniferyl alcohol, while hardwoods contain both coniferyl (50-75%) and sinapyl alcohols (25-50%). Sinapyl alcohol contains more methoxyl groups than coniferyl alcohol as shown in Fig. 2. Furthermore, the peak methanol formation rate in hardwood pulping is higher than that in softwood pulping. Ninety percent of the methanol was formed within the first 75 minutes in the

hardwood pulping processes. It took about 90 minutes to achieve 90% of the methanol in softwood pulping.

Figures. 4a and 5a also indicate that kraft pulping always yields more methanol than soda pulping does for both the hardwood and the softwood used in this study. As mentioned above, alkaline hydrolysis, as shown in reaction (1a), is the dominant methanol formation mechanism during most of a pulping process. In a kraft process, the presence of hydrogen sulfide ions can greatly facilitate delignification because of their superior nucleophilicity, as compared with hydroxyl ions. Therefore more hemicellulose and dissolved lignin are released from wood chips in the kraft pulping process. As a result, more methanol can be formed through the demethylation reactions of xylan and lignin.

According to Wilson and Hrutfiord [2], all of the ketones found in pulping, as methyl ketones, are formed through the air oxidation of extractives followed by decomposition of the extractive hydroperoxide, which undergoes a reverse alcohol condensation at a high temperature in the digester. We found in this study that the major ketone species generated in all the pulping processes were acetone and MEK. The concentration profiles of these ketones during the pulping were quite different from those of methanol as shown in Figs. 4b and 5b. In the cookings of the softwood, the profiles of acetone and MEK measured in the kraft pulping process are similar to those measured in the soda pulping, i.e., the concentrations of acetone and MEK reached a maximum at 50 minutes and then decreased after the cooking temperature reached 170°C. This behavior could be explained as a result of hemiacetals, or hemiketals, reactions between methanol and ketones [14]. Either acetals or ketals can react with methanol to form hemiacetals or hemiketals under certain conditions as follows:



Aldehyde or ketone — Hemiacetal or hemiketal (14)

which leads to a decrease in ketone concentration as cooking continues. However, some other researchers believe that the equilibrium between acetal/ketal and the corresponding aldehyde/ketone is unaffected by hydroxide [15], which contradicts the above explanation. The results also show that the acetone and MEK concentrations in the kraft hardwood pulping process did not decrease until very late in the cooking process for unknown reasons as shown in Fig. 5b. Further study is needed to understand the reaction mechanism. Figures. 4b and 5b also show that more acetone than MEK is formed in both kraft and soda pulping of a hardwood and a softwood.

It was also found that further extending the cooking process beyond 3 hours can result in a decrease in methanol and ketone concentrations, as shown in Figs. 4 and 5. The decrease in concentrations is probably related to condensation.

VOC Formation During Pulping of Kenaf

Figure. 6 shows the formation of methanol, acetone, and MEK in the soda-AQ pulping of kenaf bast and core. It was found that the cooking of kenaf core produced much more methanol than the cooking of bast. This is because kenaf core has a much higher lignin content (about 17%) than that of bast (about 7%) [16]. Kenaf does not contain hemicellulose [16], which means that all the methanol is formed through the demethylation of lignin. Therefore, the kinetic data on lignin demethylation are critical to estimate methanol formation using Eqn. (7). Unfortunately, little data about the molecular structure of kenaf lignin and lignin demethylation kinetics are available in the literature; therefore, the calculation of methanol formation during kenaf pulping was not performed. However, the experimental data does show that more methanol was formed in the pulping of kenaf core than in kenaf bast as the core has a higher lignin content than bast has.

The behaviors of ketone formation in the soda-AQ pulping of kenaf core are similar to those of kraft pulping of hardwood. The peak concentrations of ketones in bast pulping were shifted to a later pulping time compared to those in the pulping of core.

Effect of Catalyst on VOC Formation

We conducted two sets of experiments to evaluate the effect of a catalyst, anthraquinone (AQ), on VOC formation during pulping. We found that the methanol concentrations were essentially identical for the first hour of all cooking processes studied, as shown in Figs. 7 and 8. The significant differences in methanol formation with or without AQ is only at the later stage of the pulping processes when the cooking temperature is high (170°C). The catalyst increased the formation of methanol by 15% in softwood kraft pulping, as shown in Fig. 7, while an opposite phenomenon is observed in hardwood kraft pulping, i.e., the catalyst reduced the formation of methanol by about 10%, as shown in Fig. 8.

As discussed previously, methanol is formed through two mechanisms, i.e., degradation of xylans in the hemicellulose and the demethylation of lignin, as represented by reactions (1a) and (1b), respectively. According to Wilson et al. [9], xylan degradation is the dominant methanol formation mechanism. As proposed by Clayton [7], xylan degradation in alkaline pulping of wood is brought about by the conversion of 4-O-methyl-D-glucuronic acid groups present in xylans into the corresponding unsaturated acids. This postulation was later verified by Johansson and Samuelson [17]. They found that a model compound of xylan, 2-O-(4-O-methyl-D-glucopyranosyluronic acid)-D-xylitol can react with sodium hydroxide (1 M) at 150°C to yield 50% hexeneuronic acid after a 90-minute reaction time. The reaction also forms methanol at the same time. This indicates that xylans can be partially degraded and form methanol at a high pulping temperature. In pulping, the formation of methanol from xylans is mainly in the early stage of the cooking. Holton confirmed that the AQ possesses a marked capability of accelerating the delignification and leads to an increase in pulp yield [18]. On the other hand, Lowendahl and Samuelson [19] indicated that AQ has the ability to stabilize polysaccharides, such as xylan, toward alkaline degradation. Hardwood has a high xylan content (15-30%) and a low lignin content (18-25%) [11]. The effect of stabilization of xylans is probably significant enough to slow down the reaction (1a) in AQ pulping of hardwood, therefore, less methanol is formed, as shown in Fig. 8. Softwood has a low xylan content (5-10%) and a high lignin content (25-35%) [11], therefore, delignification acceleration is perhaps more significant than the stabilization of xylan degradation by AQ, producing more methanol in softwood pulping.

SUMMARIES

This report presents the concentration profiles of three major water-soluble, steam-volatile organic compounds, i.e., methanol, acetone, and MEK, during conventional pulping processes. These compounds are mainly formed in the initial stage of the cook at a temperature of 170°C. More methanol can be produced in hardwood pulping processes than in softwood. Kraft pulping processes produce more methanol than soda processes. A methanol mass balance calculation based on 100% hydrolysis of methoxyl groups in xylan indicate that hemicellulose degradation accounts for about 75% of the methanol formed in pulping. The demethylation of lignin accounts for about 20% of the methanol formed based on a ~2% lignin methoxyl group conversion given in the literature. Kinetic analysis indicates that the overall methanol formation reaction follows Arrhenius kinetics well. The formation behaviors of acetone and MEK in the processes are different from that of methanol. These ketones have probably undergone a hemiacetal or hemiketal reaction with methanol in most pulping processes. We found that wood species also contributed to the differences in the formation of these volatile compounds in pulping.

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Fig. 1

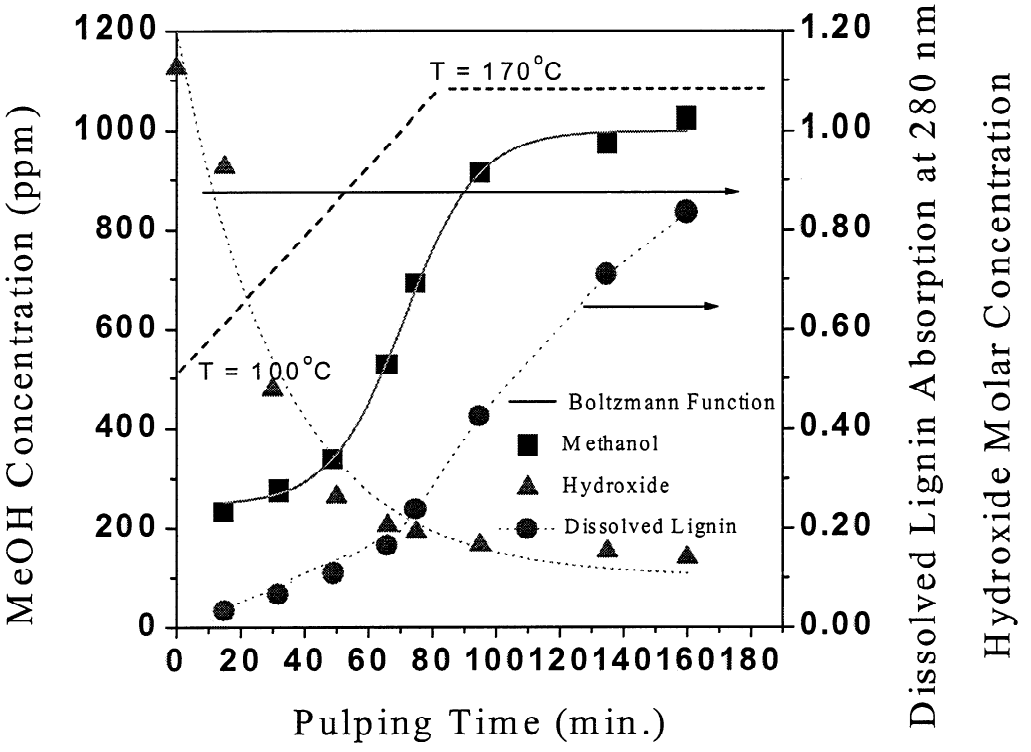
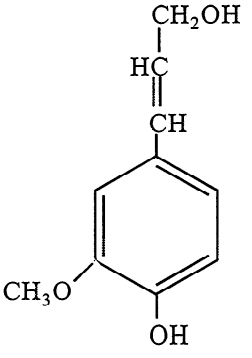
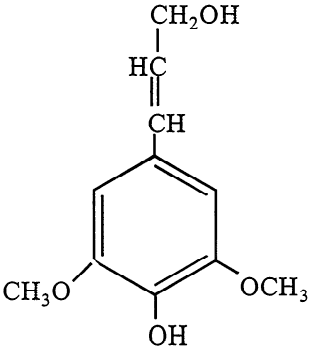


Fig. 2

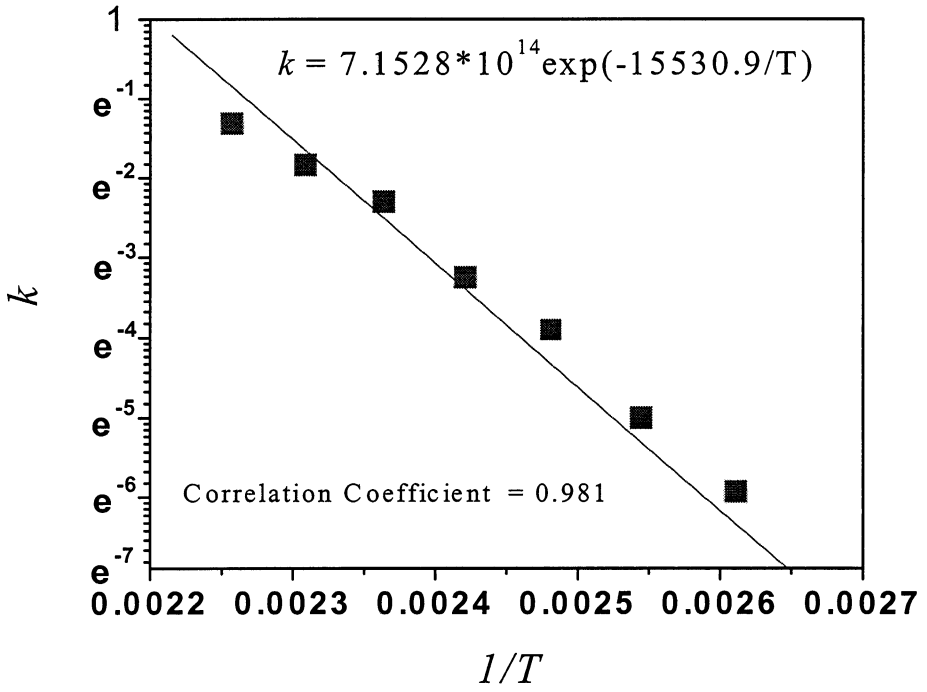


Coniferyl alcohol



Sinapyl alcohol

Fig. 3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Correlation Coefficient = 0.981
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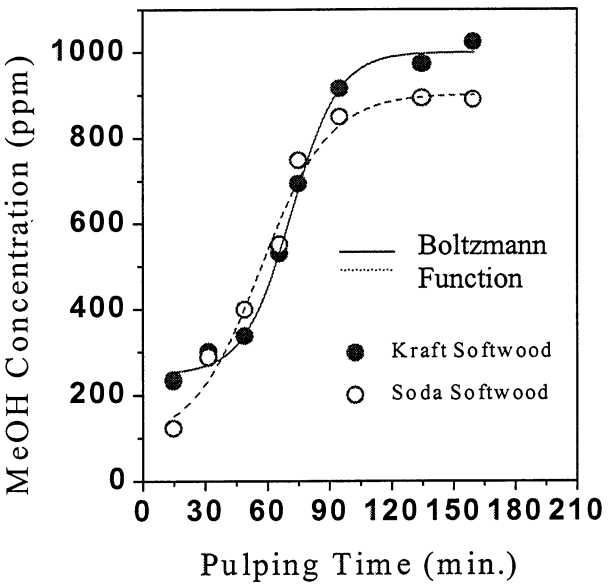
e-1
e-2
e-3
e-4
e-5
e-6
e-7
0.0022
0.0023
0.0024
0.0025
0.0026
0.0027
1/T

Fig. 4



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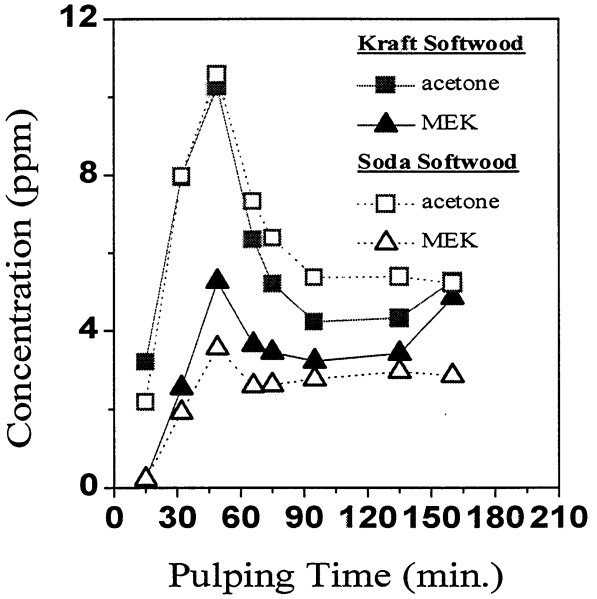
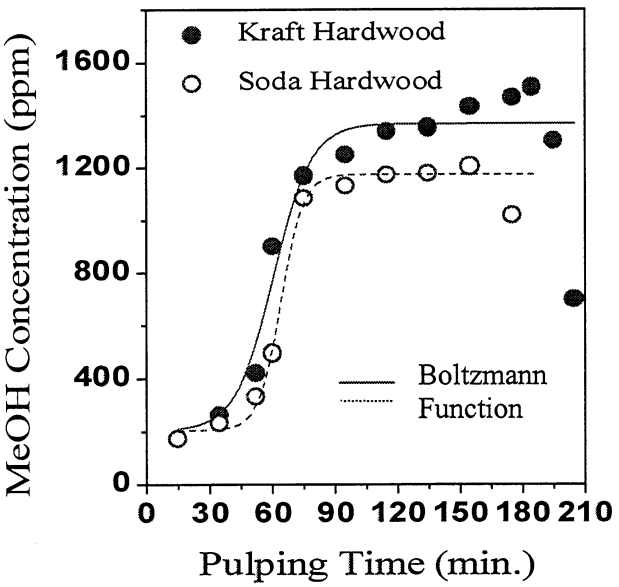


(b)

Fig. 5



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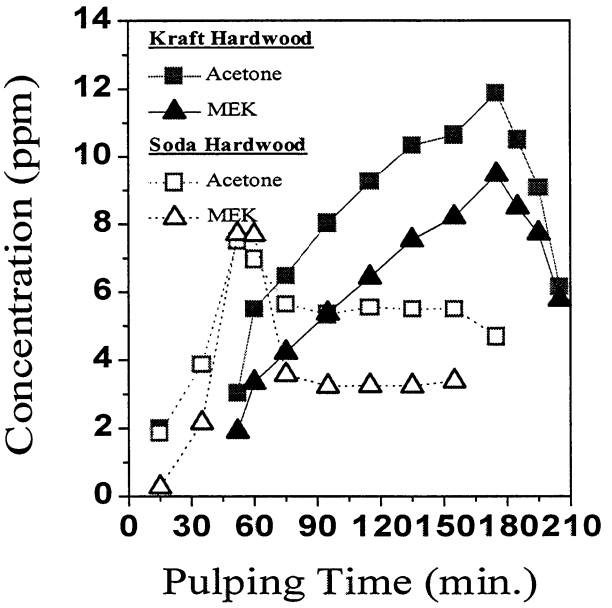
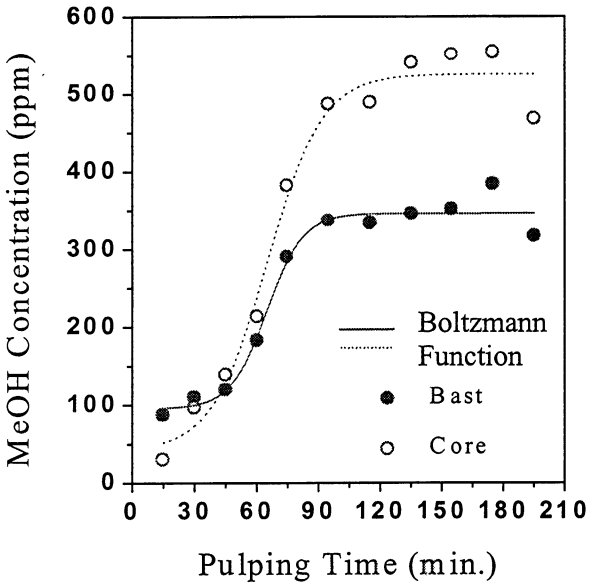


(b)

Fig. 6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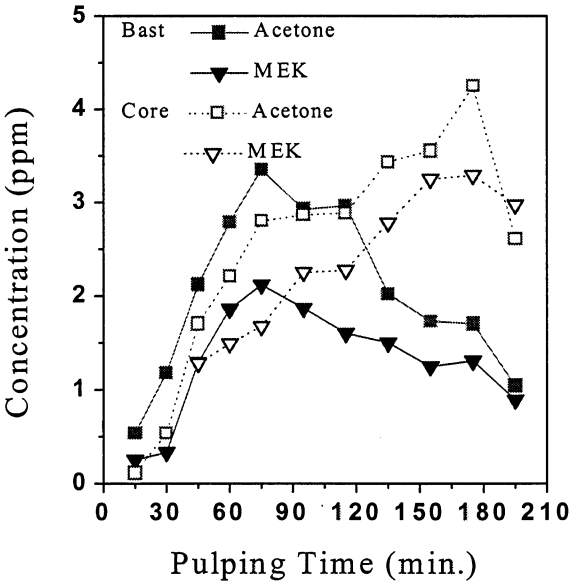
500
400
300
200
100
0
0 30 60 90 120 150 180 210
Pulping Time (min.)
Boltzmann
Function
Bast
Core

(a)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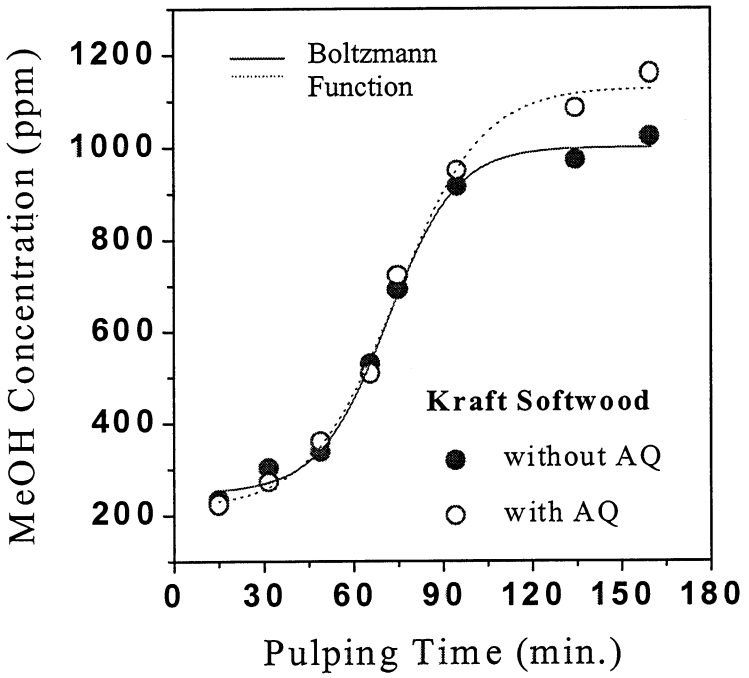
4
3
2
1
0
0 30 60 90 120 150 180 210
Pulping Time (min.)
Bast
Acetone
MEK
Core
Acetone
MEK

(b)

Fig. 7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1000
800
600
400
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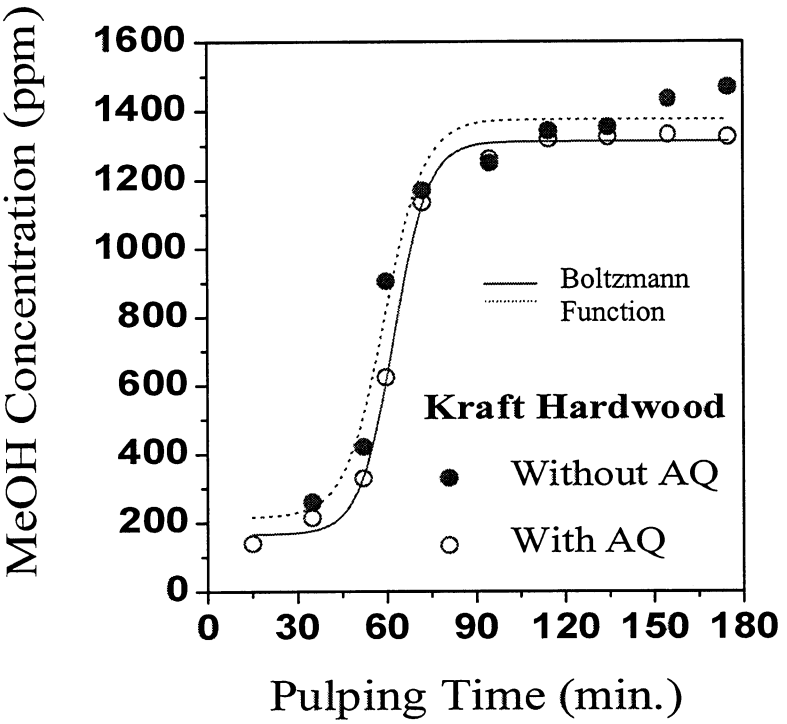
90
120
150
180
Pulping Time (min.)
Boltzmann
Function
Kraft Softwood
without AQ
with AQ

Fig. 8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1400
1200
1000
800
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200
0
0
30
60
90
120
150
180
Pulping Time (min.)
Boltzmann
Function
Kraft Hardwood
Without AQ
With AQ

Table I: A list of pulping conditions.

PARAMETERS	VALUES
Alkali (%)	18
Sulfidity (%)	0 for soda 25 for kraft
Liquid-to-Wood Ratio	4 for softwood and hardwood 8 for kenaf bast and core
Final Temperature (°C)	170
H Factor	2000
Catalyst	None and AQ for Woods AQ only for Kenaf

Table II: A list of final kappa numbers following the pulping processes.

Pulping Material	Kappa Number	
	Kraft Pulping	Soda Pulping
Softwood	28 (with AQ) 31 (without AQ)	31 (with AQ) 34 (without AQ)
Hardwood	14 (with AQ) 15 (without AQ)	16 (with AQ) 18 (without AQ)
Kenaf: Bast	N/A	8 (with AQ)
Kenaf: Core	N/A	16 (with AQ)

Table III: Calculated methanol concentrations in the final cooking liquors of birch and pine.

Parameters	Birch	Pine
Xylan content (x_{xylan})*	0.15-0.30	0.05-0.10
Ratio of 4-O-Methyl-Glucuronic Acid to xylose ($R_{me\text{-}glu\text{-}acid}$)**	0.1	0.17-0.33
Fraction of 4-O-Methyl-Glucuronic Acid hydrolyzed (f)	1.0	1.0
Calculated methanol concentration due to xylan demethylation (mg/L)***	937	781
Experimentally measured concentration in this study (mg/L)	1330	1020
Xylan demethylation contribution	70%	77%

* The average values of 0.225 and 0.075 were used in the calculation for birch and pine, respectively.

** The average value of 0.25 was chosen in the calculation.

*** The molecular weight of methanol and the 4-O-methyl-glucuronic acid of xylan are M_{MeOH} = 31 and $M_{me\text{-}glu\text{-}acid}$ =186, respectively. The liquid-to-wood ratio is R_{LW} = 4.

Table IV: Calculated methanol concentrations in the final cooking liquors of birch and pine.

Parameters	Birch	Pine
Lignin Content (x_{lignin})*	0.18-0.25	0.25-0.35
Ratio of coniferyl alcohol to lignin ($R_{Conf\text{-}alcoh}$)*	0.50-0.75	1.0
Ratio of sinapyl alcohol to lignin ($R_{Sinp\text{-}alcoh}$)*	0.25-0.50	0
Fraction of lignin demethylated (q)	q_c=0.015 q_{s1}=0.027 q_{s2}=0.027	q_c=0.015
Calculated methanol concentration due to lignin demethylation (mg/L)**	255	197
Experimentally measured concentration in this study (mg/L)	1330	1020
Lignin demethylation contribution	19%	19%

* The average values of 0.215, 0.62, and 0.38 were used for x_{lignin}, $R_{Conf\text{-}alcoh}$, and $R_{Sinp\text{-}alcoh}$, respectively, in the calculation.

** The molecular weight of methanol, coniferyl alcohol, and sinapyl alcohol are M_{MeOH} = 31, $M_{Conf\text{-}alcoh}$ =177, and $M_{Sinp\text{-}alcoh}$ =198, respectively. The liquid-to-wood ratio is R_{LW} = 4.

Table V. Methanol mass balance.

Parameters	Birch	Pine
Xylan Contribution (mg/L)	937 (70%)	781 (77%)
Lignin Contribution (mg/L)	255 (19%)	197 (19%)
Total Calculated (mg/L)	1192 (90%)	978 (96%)
Total Experimentally Measured (mg/L)	1330	1020
Unaccounted (mg/L)	138 (10%)	42 (4%)